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**Modeling of Polymer Photodegradation
for Solar Cell Modules**

**A Quarterly Technical Progress Report
Covering the Period May 1 - June 30, 1982**



A. C. Somersall and J. E. Guillet*

*** Principal Investigator**

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Department of Chemistry, University of Toronto

Toronto, Canada M5S 1A1

FSA Project, Technology Development Area

Contract Goals and Objectives

As part of the Encapsulation Task, this research program is intended to model the photodegradation of synthetic polymers used as pottants and/or cover sheets in the FSA solar cell module designs. It involves the development of a computer simulation of the chemical processes that take place under weathering conditions which could, in principle, relate directly to the performance of these materials and afford some basis for predicting and/or controlling their useful lifetimes.

The program can be divided into three main parts:

1. The development of a computer program to model the weathering/ photooxidation of an ethylene-vinyl acetate copolymer as a typical candidate for FSA applications.
2. The development of new analytical procedures for the determination of photooxidation and photodegradation at early stages in solid polymer samples.
3. The development of weathering tests suitable for use with a computer kinetic model to provide a basis for extrapolated predictions.

Summary

Any attempt to develop a technology for producing low-cost, long-life photovoltaic modules and arrays must come to terms with the weathering effects experienced by the materials exposed to the sun's ultraviolet, oxygen, moisture and the stresses imposed by continuous thermal cycling, among other things. Polymeric substances which could find application as convenient protective covers, pottants/adhesives and backcovers undergo slow, complex photooxidation which changes the chemical and physical properties of these materials. There is no good way to predict the rates of the chemical and/or physical changes which occur from accelerated tests. In part, the problem has been that there is no adequate laboratory method to measure these effects over such extended times. Furthermore, accelerated tests are of limited value in predicting rates since there is often no reciprocity between intensity and time of exposure.

An alternative approach developed in our laboratories has been to simulate the process of photooxidation with a computer model which could be verified with experimental data from accelerated and outdoor exposures. The model now consists of a set of 32 reactions (Table I) for the basic reaction sequence based on the now well established mechanism of hydrocarbon oxidation. Rate parameters have been assigned to these fundamental equations, based on our best estimates from the literature (Table I). A problem with such a simulation study is that the predicted rates will be only as reliable as the rate parameter data base employed. We anticipate continuous refinement of this data base in further work.

Early computer modeling results have shown that the processes of photooxidation involve a long induction period, of up to several years in the pure hydrocarbon, followed by a fairly rapid deterioration. Initiation is effected fortuiously in the program by assigning a low rate constant for R-H cleavage or using low initial concentrations (ca. 10^{-4} M) for either ketone or

hydroperoxide moieties. The principal products of photooxidation are ketones, alcohols, water and alkenes, with smaller quantities of aldehydes, acids, carbon monoxide, etc.

During the past quarter we have tried to readdress two major considerations of much importance to our mechanistic model.

1. The Rate of Initiation

We have used in earlier results the value of $k_i = 0.3 \times 10^{-5} \text{ s}^{-1}$ and $0.3 \times 10^{-4} \text{ s}^{-1}$ for the rate of photon absorption by the ketone and hydroperoxide chromophores. This may be rationalized as follows.

$$I'(\text{absorbed}) = I'(\text{incident}) - I'(\text{transmitted})$$

$$\begin{aligned} I'_a &= I'_0 - I'_t \\ &= I'_0 - I'_0 e^{-\epsilon c l} \\ &= I'_0 \epsilon c l \quad \text{per unit area} \end{aligned}$$

$$\text{Total } I(\text{absorbed}) = I'_a A \quad \text{for a rectangular sample, depth } l$$

$$\begin{aligned} I_a &= I'_0 \epsilon c l A \\ &= I'_0 \epsilon c V \end{aligned}$$

\therefore The number of Einsteins absorbed per unit volume (cm^3)

$$E_a = I_a / V = I'_0 \epsilon c$$

For $I_a = E$ (Einsteins)

$$V = \text{cm}^3 = 10^{-3} l$$

$$\epsilon = l \text{ mol}^{-1} \text{ cm}^{-1}$$

$$I_0 = E \text{ cm}^{-2}$$

$$c = \text{mol } l^{-1}$$

E_a (Einsteins absorbed)

$$= 1000 I_0 \epsilon c$$

$$\therefore k_i = E_a / c = 1000 I_0 \epsilon$$

$$= 0.3 \times 10^{-5} \text{ s}^{-1}$$

$$I_0 (313 \text{ nm}) = 3 \times 10^{-9}$$

$E \text{ cm}^{-2} \text{ s}^{-1}$ for typical optical bench in our lab

$$\epsilon(313 \text{ nm}) \sim 1 - 10 \text{ for ketones}$$

This measure of the number of Einsteins absorbed per unit volume may be inappropriate for thin films.

Rather, if we consider a film of thickness 0.1 cm the rate of photon absorption may be given simply by

$$\begin{aligned}
 I_{\text{abs}} &= I_0 \epsilon c \ell & I_0 &= 4.0 \times 10^{-9} \text{ E cm}^{-2} \text{ s}^{-1} \text{ for} \\
 \therefore k_i &= I_{\text{abs}}/c & & \text{integrated overlap of solar spectrum} \\
 &= I_0 \epsilon \ell & & \text{with the absorption spectrum of 2-} \\
 &= 4 \times 10^{-9} \times 5 \times 0.1 & & \text{butanone or tBuOOH.} \\
 &= 0.2 \times 10^{-8} \text{ s}^{-1} \text{ for ketones} & & \epsilon (\text{overlap average}) \sim 5 \\
 k_i &= 0.4 \times 10^{-9} \text{ s}^{-1} \text{ for hydroperoxides}
 \end{aligned}$$

We have now substituted these latter values for the photochemical reactions in the mechanism.

2. The Rate of Termination

We have used in earlier results the value of $k_t = 0.2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for the key bimolecular termination reaction of peroxy radicals. The rationale has been that termination occurs in local "cages" with limited diffusion of these polymeric radicals and over such short range, we have considered the process to be not much unlike diffusion in viscous liquids.

However, the rate of termination in polypropylene has been measured at 25 °C, $k_t = 1 - 8 \text{ M}^{-1} \text{ s}^{-1}$ [Gorton, Carlsson and Wiles, *Macromolecules*, 12, 1071 (1979)]. They examined the decay of peroxy radicals by esr in photo-oxidized films upon cessation of irradiation. The value at 45 °C given by Mayo [Mayo, *Macromolecules*, 11, 942 (1978)] could be an order of magnitude higher when derived from thermal oxidation kinetics. In any case, both evidences point to a much slower rate for peroxy radical termination in polypropylene.

We have therefore changed the value to $k_t = 10^1 \text{ M}^{-1} \text{ s}^{-1}$ for the bimolecular processes limited by diffusion in the polymer matrix.

Results

To slow down termination in effect increases the kinetic chain length and we find complete oxidation at the high initiation rates in less than two days. The major products are unchanged.

However, when the rate constant for initiation is reduced (to about 10^{-9}) and the initiator concentration is correspondingly increased, we observe complete oxidation over a five-year period. However, there is no apparent induction phase since the change is almost linear over time. At intermediate values of initiation (10^{-8}) the process is again near linear and takes up to 215 days.

Much work remains to be done in refinement of the model to allow for the inclusion of substituent groups, the reactivity of secondary and tertiary C-H bonds, the significance of diffusion, the influences of temperature cycling and dark reactions, and the impact of additives. However, these modeling studies which can, in principle, simulate real systems represent a novel approach to the general understanding of polymer photooxidation phenomena which should lead to new understanding in the study of controlled lifetimes for polymers and for the development of procedures which would allow the prediction of performance of plastics for solar applications.

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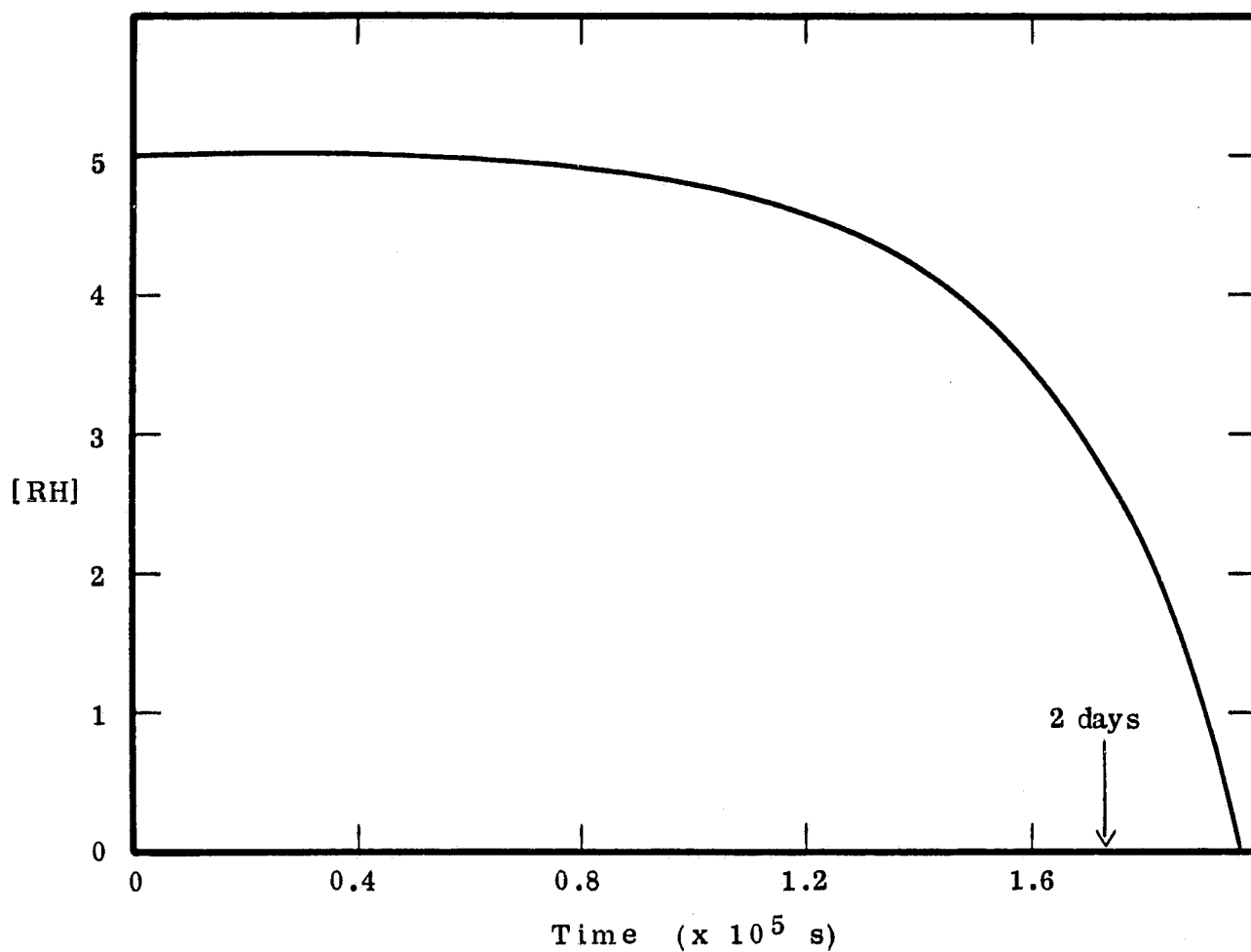


FIGURE 1. Photooxidation with "high" intensity (UV).
 $[C=O]_{init} 10^{-6} \text{ M}$. $k_i = 0.3 \times 10^{-5} \text{ s}^{-1}$. $k_t = 10^1 \text{ M}^{-1} \text{ s}^{-1}$.

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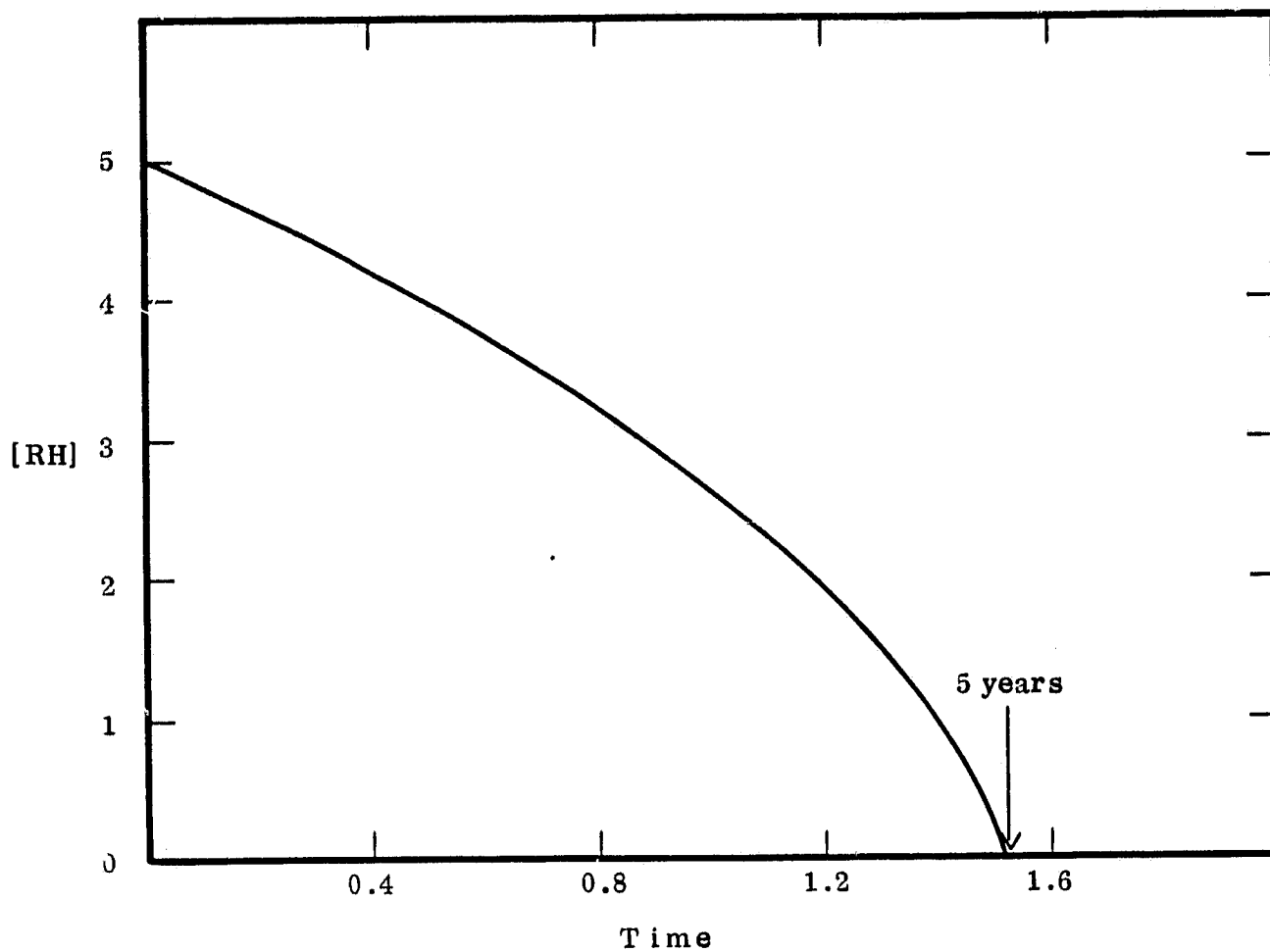


FIGURE 2. Photooxidation with "low" intensity (UV). $[C=O]_{init} 10^{-4} M$.
 $k_i = 0.2 \times 10^{-8} s^{-1}$. $k_t = 10^1 M^{-1} s^{-1}$

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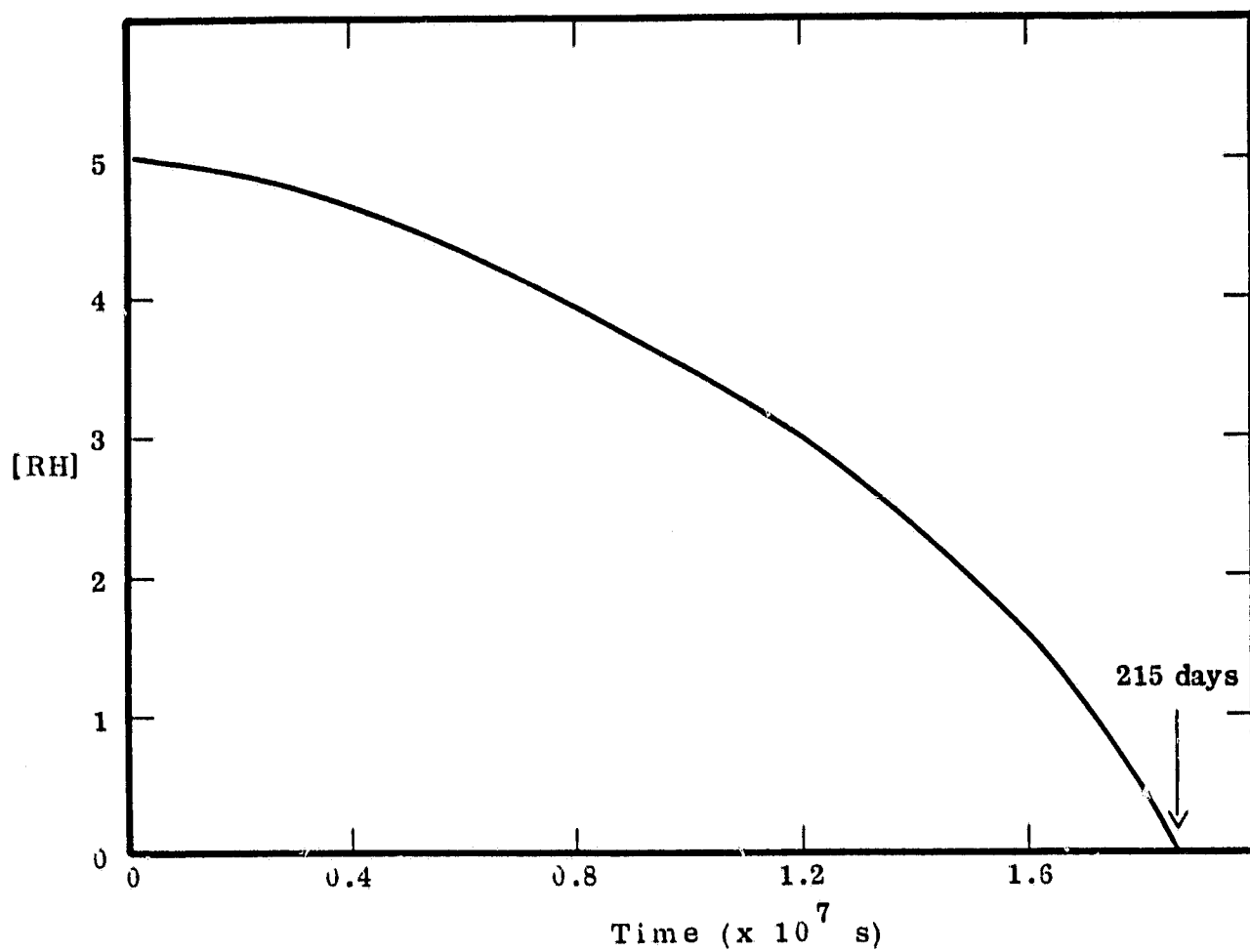


FIGURE 3. Photooxidation with "intermediate" intensity UV.

$[C=O]_{init} 10^{-5} M$. $k_i = 0.2 \times 10^{-7} s^{-1}$. $k_t = 10^1 M^{-1} s^{-1}$.